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The geometric isomers of methyl-2,4,6-decatrienoate, including pheromones of at least two species of stink bugs

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Abstract—All eight geometric isomers of methyl 2,4,6-decatrienoate were synthesized from readily accessible starting materials by fully exploiting Wittig-type olefinations, and taking advantage of an easy separation of 2*E* and 2*Z* unsaturated esters. The aggregation pheromone of the brown-winged green bug, *Plautia stali*, methyl (*E*,*E*,*Z*)-2,4,6-decatrienoate (also a cross-attractant for the brown marmorated stink bug, *Halyomorpha halys*), was expediently produced in two easy steps from (*E*)-4,4-dimethoxy-2-butenal in 55% yield. The sex pheromone of the red-shouldered stink bug, *Thyanta pallidovirens*, methyl (*E*,*Z*,*Z*)-2,4,6-decatrienoate, was conveniently synthesized from 2,4-octadiyn-1-ol in 32% yield using in situ manganese dioxide oxidation–Wittig condensation in a key step.
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1. Introduction

2,4,6-Decatrienoic acid does not appear to commonly occur in nature. Mixtures of several geometric isomers esterified with diterpenols and triterpenols have been found in the lattices of several *Euphorbia* plant species,[1–3] with the *E*,*E*,*Z* isomer being perhaps the most abundant. Methyl (*E*,*Z*,*Z*)-2,4,6-decatrienoate (**10**) was identified as a thermally unstable male-produced sex pheromone of the red-shouldered stink bug, *Thyanta pallidovirens*.[3,4] Methyl (*E*,*E*,*Z*)-2,4,6-decatrienoate (**3**) was isolated from males of the brown-winged green bug, *Plautia stali*, and was demonstrated to be responsible for the aggregation of conspecific males and females in orchards.[5] Reports indicated that yet another bug, the brown marmorated stink bug, *Halyomorpha halys*, was cross-attracted to ester **3** in field trials.[6,7] Although the explanation of this cross-attraction is still unknown, the trapping of *H. halys* with ester **3** was of particular interest to us because this invasive bug has recently become established in the Northeast U.S. and poses a potential threat to many commercial crops and ornamental plants.[8] The availability of an attractant for monitoring the spread of *H. halys* in the U.S. would be invaluable to extension and pest management programs.

Our preliminary studies showed that *H. halys* was cross-attracted to not only the *E*,*E*,*Z* ester **3** but also to the *E*,*Z*,*Z* ester **10**, and, importantly, that both esters readily isomerized under daylight to produce primarily mixtures of geometric isomers. The most attractive blend of esters for *H. halys* is yet to be found, so easy access to ester **3** and other isomers is a prerequisite for our future biological studies. Synthesis of ester **3** as an attractant for *P. stali* was patented in Japan[9] and used a partial hydrogenation of methyl (*E*,*E*)-2,4-decadien-6-ynoate with Lindlar catalyst in a key step. Not only was the starting material not readily available, the yield of **3** from the reduction step was only 12%. To our knowledge, the only other reported preparation of ester **3** produced it as a by-product in an unspecified yield.[10] The existing synthesis of ester **10** featured a one-pot double-carbocupration of acetylene with subsequent additon of methylpropiolate and provided the desired compound in 13% yield after reverse phase HPLC purification.[3]

In this paper, we report syntheses of all geometric isomers of methyl 2,4,6-decatrienoate by fully exploiting Wittig-type olefinations. Two stink bug pheromones, **3** and **10**, were conveniently prepared in 55 and 32% yields from easily accessible starting materials, (*E*)-4,4-dimethoxy-2-butenal and 2,4-octadiyn-1-ol, respectively.

2. Results and discussion

2.1. Synthesis of 4*E* isomers

All four isomers with a 4*E* configuration were easily synthesized from the same precursor, (*E*)-4,4-dimethoxy-2-butenal (**1**). The starting material for the preparation of **1**,

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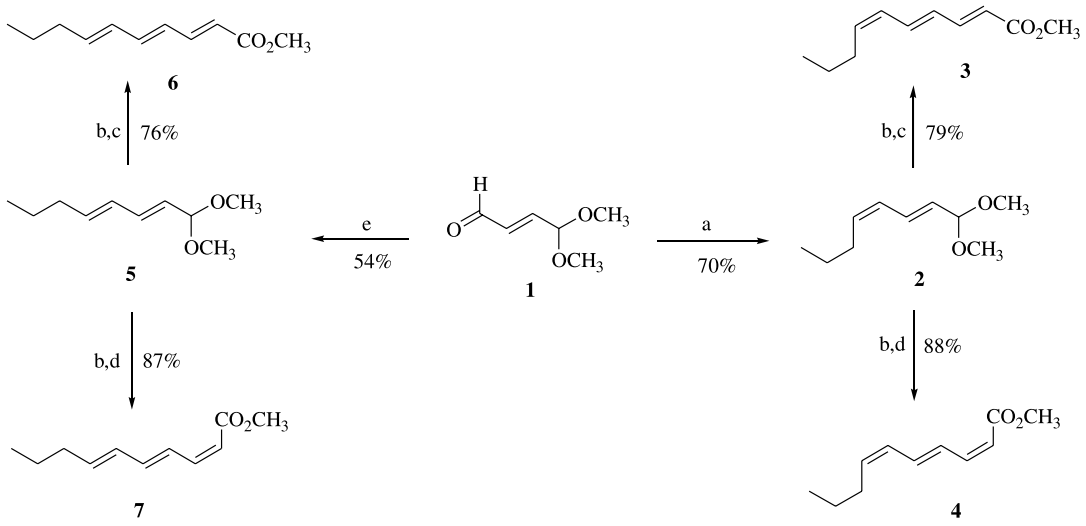


Scheme 1. Reagents and conditions: (a) $(Ph_3PC_4H_9)Br/[(CH_3)_3Si]_2NNa$, −70 °C; (b) PTSA, acetone–H_2O, 0–5 °C; (c) $(CH_3O)_2P(O)CH_2CO_2CH_3$, K_2CO_3–H_2O; (d) $(CF_3CH_2O)_2P(O)CH_2CO_2CH_3/[(CH_3)_3Si]_2NK$, 18-crown-6, −70 °C; (e) $(Ph_3PC_4H_9)Br/2BuLi$, THF.

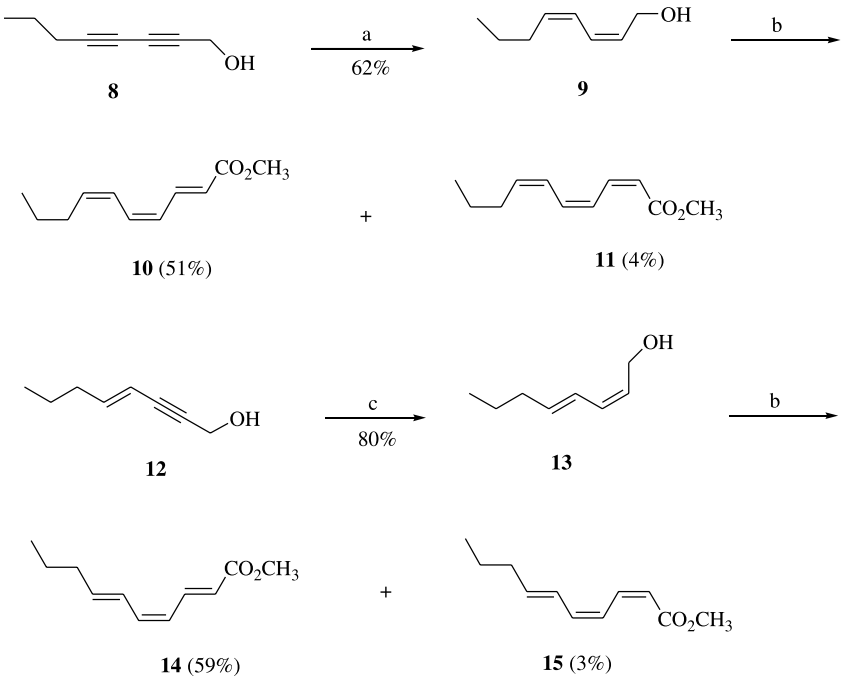
fumaraldehyde bis(dimethylacetal), is commercially available, or can be straightforwardly prepared from furan.[11] Earlier, we used this compound in the syntheses of conjugated dienic insect pheromones using stereoselective Wittig olefination.[12] In fact, this approach has already been applied to make the acetals **2** and **5**,[13] key intermediates in this synthesis. For *cis*-olefination of **1**, we deprotonated *n*-butyltriphenylphosphonium bromide with bis(trimethylsilyl)amide; condensation with **1** provided a 70% yield and a 96:4 ratio of **2** and **5**. *Trans*-olefination of **1** was accomplished by using 2 equiv of butyllithium as the base[14] and gave a 54% yield with a 94:6 ratio of **5**:**2**. Acetals **2** and **5** were deprotected under mild conditions (*p*-TSA, acetone-water, 0–5 °C) to avoid *cis-trans* isomerizations[12,13] and the unsaturatred aldehydes were used in the next steps without purification. A Horner–Wadsworth–Emmons *trans*-olefination with trimethyl phosphonoacetate was employed to convert **2** and **5**, respectively, to esters **3** and **6**. We selected the most straightforward, solvent-free protocol using potassium carbonate in water[15] and obtained a 79% yield for ester **3** (**3**:**6**, 96:4) and 76% yield for **6** (**6**:**3**, 95:5). The condensations were not entirely *trans*-stereoselective, but the minor *cis*-olefination products were successfully separated by flash chromatography on SiO_2. Importantly, the configurations of the existing double bonds in **2** and **5** essentially did not change during the course of the reaction, though we did find it useful to protect the reaction vessels from light to avoid photo-induced isomerizations. Whereas 2*E* olefinic esters could be easily prepared from aldehydes, there are not many procedures to reliably make 2*Z* olefinic esters. We were pleased to find that dienic aldehydes made from acetals **2** and **5** could be converted to esters **4** and **7** with *cis*-stereoselectivity under the modified Horner–Wadsworth–Emmons olefination[16] conditions utilizing electrophilic $(CF_3CH_2O)_2P(O)CH_2COOCH_3$ and a strongly dissociated base system, $KN(TMS)_2$/18-crown-6. The yields of the esters **4** and **7**, after purification from trace amounts of 2*E* esters by flash chromatography, were 88 and 87%, respectively, and the stereochemical purities (% of **7** in **4** and vice versa) 93 and 95%, respectively. Some loss of the geometry (from 96 to 93%) of the 6*Z* double bond in **4** was perhaps due to using a fairly large amount of 18-crown-6 (5 equiv). This could significantly increase the polarity of the medium and promote *cis-trans* isomerizations of the existing double bonds in the aldehyde.[17] Despite this minor limitation, the *cis*-olefination method seems viable for syntheses of **4** and **7** because of high yields and availability of all components (Scheme 1).

2.2. Synthesis of 4*Z* isomers

For syntheses of the isomers with 4*Z* double bonds, we intended to utilize the same strategy that had been successful for 4*E* isomers: that is, to assemble the sensitive trienoic esters in the last step by capitalizing on high yielding stereoselective *cis* and *trans* Horner-Wadsworth–Emmons olefinations. The main challenge of this pathway was the instability of the intermediate 2*Z* dienals, which were expected to be even more labile than *Z*-enals, which are themselves known to undergo rapid isomerizations[18] (Scheme 2).

Octadiyn-1-ol (**8**) was converted to a THP–ether and hydroborated with dicyclohexylborane[19] to furnish, after protonolysis and deprotection, dienol **9** in 62% yield and 99% selectivity. First, we examined a sequential one-pot Swern oxidation–Wittig reaction protocol that has proved useful for unstable aldehydes.[20] The oxidation of dienol **9** was conducted under standard Swern oxidation conditions (see Section 3), followed by the addition of methyl (triphenylphosphoranylidene)acetate to provide esters **10** and **11** which were separated by flash chromatography. Whereas the by-product all-*cis* isomer **11** was sufficiently pure to be fully characterized by ^1H and ^{13}C NMR spectra, ester **10** was significantly (~15%) contaminated with isomer **3**, judged by ^1H NMR (δ 6.84 and 7.35).

We next explored an in situ alcohol oxidation–olefination reaction utilizing manganese dioxide and a stabilized Wittig reagent, which reportedly proceeded without a change of the geometry of a pre-existing *Z* double bond in starting allylic alcohols.[21] Oxidation of **9** with activated MnO_2 was



Scheme 2. Reagents and conditions: (a) DHP, PPTS/dicyclohexylborane/AcOH/MeOH, PPTS; (b) MnO_2, CH_2Cl_2, $(Ph)_3P{=}CHCO_2Me$; (c) Zn(Cu/Ag), MeOH–H_2O.

conducted in the presence of methyl (triphenylphosphoranylidene)acetate in methylene chloride[21] and gave a mixture of esters (70% yield) separated by flash chromatography into individual stereoisomers **10** (51%) and **11** (4%). ^1H and ^{13}C NMR spectra of **10** were in close agreement with literature values.[3] Ester **10** was unstable under GC conditions[3,22] to asses its purity but the ^1H NMR spectrum revealed only traces (total 3–5%) of esters **3** and **14** (δ 6.27). A slight isomerization of 4*Z* or 6*Z* double bonds may have occurred during the course of olefination of the intermediate (*Z*,*Z*)-2,4-octadienal, which appeared to be a limiting step and required a 12 h reaction time at room temperature with 20% excess of the Wittig reagent. (Attempts to invigorate the olefination by increasing the temperature to 40 °C, or using THF instead of CH_2Cl_2, resulted in lower yields and decreased stereochemical purity of ester **10**). Thus, the in situ version of alcohol **9** oxidation–Wittig reaction proved efficient for synthesis of ester **10**, the pheromone of *T. pallidovirens*, because of its simplicity and reasonably good overall yield (32%) from the known diyne alcohol **8**.

The second part of Scheme 2 depicts the syntheses of the remaining two 4*Z* esters **14** and **15**. A CuI/$[(Ph)_3P]_4Pd$ catalyzed condensation[23] of (*E*)-1-iodo-1-pentene[24] with propargyl alcohol provided enynol **12** in 69% yield. Partial *cis*-hydrogenation of **12** was accomplished in 80% yield and >98% stereoselectivity using a Zn(Cu/Ag) reagent that proved handy in the reduction of enynols.[25] Dienol **13** underwent in situ MnO_2 oxidation–Wittig reaction similar to **9** and furnished esters **14** and **15** in 59 and 3% yields, respectively. Ester **15** was 93% pure and was contaminated with esters **7** and **14**, and ester **14** was 96% pure by GC. Despite appearing as a by-product, isomer **15** was sufficiently pure (as was ester **11**) to be fully characterized by ^1H and ^{13}C NMR. Because esters **11** and **15** were not target molecules and will be required as reference compounds in our bioassays, we did not pursue more economical synthetic routes. (An attempted synthesis of **15** by oxidation of **13** with MnO_2 and *cis*-olefination of the crude aldehyde with a fluorinated Horner–Wadsworth–Emmons reagent, as described above, resulted in a product of 88% stereochemical purity).

The structure assignments of the geometric isomers of methyl 2,4,6-decatrienoate were based on the expected ^1H chemical shifts, ^1H–^1H coupling constants, and specifically ^1H–^1H COSY NMR recordings. In general, interactions of vicinal protons across double bonds were of expected values, with J_{cis}=11.0–12.1 Hz, and J_{trans}=14.7–15.5 Hz. Yet, in the *E*,*Z*,*Z* isomer **10**, *cis* coupling constants J_{4-5} and J_{6-7} were anomalously low, 9.4 and 9.1 Hz, respectively.

All stereoisomeric methyl 2,4,6-decatrienoates but one (**10**[3]) survived GC conditions, as judged by the integrity and sharpness of their peaks and a close similarity of their mass spectra in the GC-MS analyses. Besides a strong molecular ion at *m*/*z* 180 (39–71%), they display a notable peak at 149 *m*/*z* (11–26%) apparently due to $(M\text{-}OCH_3)^+$ ion. However, the GC and GC–MS analyses of ester **14** performed at the injection temperature 260 °C showed an additional peak with a significantly shorter retention time but the same molecular ion (180 *m*/*z*) as the main compound, and thus could be misleading in the determination of its purity. However, at lower injection temperatures (e.g., 130 °C) the extra peak (apparently arising from an intramolecular Diels–Alder reaction) was absent. Although we did not pursue methodical photochemical studies, all geometric isomers of methyl 2,4,6-decatrienoates seemed unstable under daylight, not surprising given a strong UV absorption at ~300 nm (see Section 3). Thus, the attractant of *H. halys*, *E*,*E*,*Z*-ester **3**, left unprotected under

room conditions as a hexane solution (1 mg/mL) in a Pyrex vial for two days decreased in purity from 95 to 78%, with *Z*,*E*,*Z*-ester **4** and *E*,*E*,*E*-ester **6** being the main by-products. A similar trend was noticed when rubber septa impregnated with ester **3** were exposed to sunlight. The pheromone of *T. pallidovirens*, *E*,*Z*,*Z*-ester **10**, both in a hexane solution and rubber septa formulations, isomerized in sunlight producing a mixture of geometric isomers, among which esters **3** and **6** were most abundant. The role of esters **3** and **10**, or their combinations with other isomers, in trapping *H. halys* stink bug is under investigation.

3. Experimental

3.1. General

Boiling points are uncorrected. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ with TMS as an internal standard on a Bruker QE-300 spectrometer. Chemical shifts are reported in δ, and J coupling constants in Hz. ^{1}H–^{1}H COSY was used to assign signals of trienoates. GC analyses were performed on a Shimadzu 17A gas chromatograph with a flame ionization detector using a 60 m×0.25 mm RTX-1701 column (Restek Corporation), or a 15 m×0.25 mm DB-5 column (J&W Scientific), and H_2 as carrier gas. Electron impact ionization mass spectra (70 eV) were obtained with an Agilent Technologies 5973 GC-MS equipped with a 30 m× 0.25 mm HP-5MS column. High resolution electron impact mass spectra were measured on a Shimadzu GC-17A coupled with JEOL JMS-SX102A mass spectrometer using a 15 m×0.25 mm OV-5 capillary column (Ohio Valley Specialty Chemicals, Marietta, OH). UV spectra were recorded in hexane on a Shimadzu UV-160 spectrophotometer. Flash chromatography was carried out with 230–400 mesh silica gel (Whatman), and neutral alumina (Brockman Activity I, 60–325 mesh, Fisher Scientific, acetals **2** and **5**). The reagents were purchased from Aldrich Chemical Co. unless otherwise specified. THF was freshly distilled from sodium-benzophenone ketyl under N_2. Methylene chloride and benzene were distilled from P_2O_5. (*E*)-4,4-dimethoxy-2-butenal (**1**) was prepared from (*E*)-1,1,4,4-tetramethoxy-2-butene.[11] Mention of a proprietary company or product does not imply endorsement by the U.S. Department of Agriculture.

3.1.1. (*Z*,*E*)-2,4-Octadienal dimethyl acetal (2). To a suspension of butyltriphenylphosphonium bromide (7.98 g, 20 mmol) in dry THF (30 mL) was added a THF solution of sodium bis(trimethylsilyl)amide (20 mL of 1.0 M, 20 mmol) at −40 °C. The mixture was allowed to warm to room temperature, stirred for 2 h, and then cooled to −75 °C. Aldehyde **1** (2.860 g, 22 mmol) dissolved in dry THF (10 mL) was slowly added while maintaining the temperature between −75 and −65 °C. The resulting mixture was stirred at this temperature for 2 h and warmed to rt. The mixture was poured into ice-water, extracted with hexane/ether, 1:1, and dried (Na_2SO_4). Evaporation of the solvent and flash chromatography with hexanes/ethyl acetate, 95:5, afforded **2** (2.370 g, 70%) consisting of 92% **2**, 3% *E*,*E*-acetal **5** and 3% of the deacetalization product, (*Z*,*E*)-2,4-octadienal. No deacetalization was observed when chromatography was conducted on neutral alumina (Brockman Activity I, 60–325 mesh, Fisher Scientific) as described.[12] MS (*m*/*z*): 170 (M^+, 35), 141 (34), 139 (100), 127 (81), 109 (40), 97 (57), 88 (59), 79 (63), 67 (46), 45 (52). ^{1}H NMR: 0.91 (t, J=7.3 Hz, H-8), 1.41 (sextet, J= 7.3 Hz, H-7), 2.17 (dtd, J=7.3, 7.3, 1.1 Hz, H-6), 3.32 (s, 6H, OCH_3), 4.85 (br d, J=4.9 Hz, H-1), 5.50 (dt, J=10.5, 7.5 Hz, H-5), 5.59 (dd, J=15.6, 4.9 Hz, H-2), 6.00 (br dd, J=11.0, 11.0 Hz, H-4), 6.63 (dd, J=15.5, 11.0 Hz, H-3). The data are a close match with reported values.[13]

3.1.2. (*E*,*E*)-2,4-Octadienal dimethyl acetal (5). To a suspension of butyltriphenylphosphonium bromide (1.197 g, 3 mmol) in dry THF (10 mL) was added butyllithium (1.2 mL, 2.5 M in hexanes, 3 mmol) at −40 °C. The mixture was stirred 2 h at −20 to (−30) °C, cooled to −65 °C, and treated with a solution of aldehyde **1** (390 mg, 3 mmol) in THF (3 mL). After decolorization, the second equivalent of BuLi (1.2 mL) was added at −65 °C, and the dark-brown mixture was allowed to warm to −40 °C. After stirring 1 h, methanol (200 μL) was added and the mixture was poured into water and extracted with hexanes/ether, 1:1. The organic extracts were washed with NH_4Cl solution, water, dried, and concentrated. Flash chromatography on neutral alumina with 2% ethyl acetate in hexanes afforded **5** (276 mg, 54%) of 98% chemical purity and **5**:**2** ratio 94:6. ^{1}H NMR: 0.89 (t, J=7.5 Hz, H-8), 1.41 (sextet, J=7.3 Hz, H-7), 2.06 (br dt, J=6.8, 7.2 Hz, H-6), 3.31 (s, 6H, OCH_3), 4.80 (br d, J=4.9 Hz, H-1), 5.50 (dd, J=15.5, 5.0 Hz, H-2), 5.75 (dt, J=15.1, 6.8 Hz, H-5), 6.04 (br dd, J=15.1, 10.2 Hz, H-4), 6.31 (dd, J=15.5, 10.2 Hz, H-3). The data are in close agreement with those reported.[13]

3.1.3. Methyl (*E*,*E*,*Z*)-2,4,6-decatrienoate (3). Acetal **2** (2.125 g, 12.5 mmol) was stirred with *p*-toluenesulphonic acid monohydrate (47 mg, 0.25 mmol) in a water–acetone (5 mL+13 mL) solution at 0–5 °C. After 0.5 h, dry potassium carbonate (~500 mg) was added to bring the pH to ~9–10. The mixture was evaporated on a rotary evaporator, extracted with hexane/ether, 3:1, dried (Na_2SO_4) for 0.5 h, and concentrated to give crude (*Z*,*E*)-2,4-octadienal (1.570 g). This was added to a mixture of trimethyl phosphonoacetate (3.035 mL, 18.75 mmol), potassium carbonate (4.174 g, 30.2 mmol) and water (3 mL). The mixture was stirred at rt overnight protected from light by wrapping the flask in an aluminum foil. The mixture was diluted with water, extracted with hexanes/ether, 1:1, the organic extract was washed with brine and dried. After evaporation of the solvent, the crude product was purified by flash chromatography with hexanes/ethyl acetate, 95:5. A low-polar fraction (27 mg, 92% *Z*,*E*,*Z*-ester **4**, 6% **7**, and 2% **3**) was isolated followed by the main fraction (1.784 g, 79%), **3**:**6**, 96:4. MS (*m*/*z*): 180 (M^+, 53), 151 (9), 149 (19), 138 (18), 121 (22), 120 (16), 119 (44), 111 (20), 107 (27), 106 (15), 105 (19), 91 (83), 79 (100), 77 (38). ^{1}H NMR: 0.92 (t, J=7.2 Hz, H-10), 1.43 (sextet, J=7.3 Hz, H-9), 2.21 (qd, J=7.4, 1.3 Hz, H-8), 3.73 (s, OCH_3), 5.68 (dt, J=10.6, 8.0 Hz, H-7), 5.86 (d, J=15.5 Hz, H-2), 6.09 (br dd, $J_1 \sim J_2$=11.0 Hz, H-6), 6.28 (dd, J=14.7, 11.4 Hz, H-4), 6.84 (dd, J=14.7, 11.3 Hz, H-5), 7.35 (dd, J=15.1, 11.3 Hz, H-3). ^{13}C NMR: 13.7 (C-10), 22.7 (C-9), 30.1 (C-8), 51.4 (OCH_3), 120.0, 128.1, 129.6, 136.1, 137.6, 145.0

(C-2–C-7), 167.5 (CO_2CH_3). UV: λ_{max} 295 nm (ε 45716). ^{1}H NMR and mass-spectrum of **3** were in a close agreement with reported.[5]

3.1.4. Methyl (*Z,E,Z*)-2,4,6-decatrienoate (4). Bis(2,2,2-trifluoroethyl) (methoxycarbonylmethyl)phosphonate (954 mg, 3 mmol), 18-crown-6 (3.96 g, 15 mmol) and dry THF (40 mL) were loaded into the flask, and the mixture was cooled to −70 °C. Potassium bis(trimethylsilyl)amide (6.0 mL, 0.5 M in toluene, 3 mmol) was added, and the pale-yellow suspension was stirred for 15 min at this temperature. Crude (*Z,E*)-2,4-octadienal, prepared from acetal **2** (510 mg, 3 mmol) as described in the previous experiment, was dissolved in 5 mL THF and added to the reaction mixture at −75 °C. The mixture was stirred for 1 h (or until GC analysis showed completion of the reaction) at that temperature, poured into saturated NH_4Cl solution, extracted with ether/hexanes, 1:1, then the organic layer was washed with water, dried, concentrated, and flash chromatographed with hexanes/ethyl acetate, 97:3. (*Z,E,Z*)-ester **4** (473 mg, 88%) containing 7% (*Z,E,E*)-ester **7** was isolated from a low-polar fraction. MS (*m/z*): 180 (M^+, 60), 151 (13), 149 (26), 138 (30), 121 (29), 120 (20), 119 (61), 111 (25), 107 (30), 106 (17), 105 (22), 91 (88), 79 (100), 77 (38). ^{1}H NMR: 0.92 (t, J=7.3 Hz, H-10), 1.43 (sextet, J=7.2 Hz, H-9), 2.22 (br q, J=7.3 Hz, H-8), 3.72 (s, OCH_3), 5.63 (d, J=11.0 Hz, H-2), 5.68 (dt, J=11.0, 7.5 Hz, H-7), 6.18 (br dd, $J_1 \sim J_2$=11.0 Hz, H-6), 6.64 (dd, $J_1 \sim J_2$=11.3 Hz, H-3), 6.78 (dd, J=15.1, 11.4 Hz, H-5), 7.47 (dd, J=15.0, 11.5 Hz, H-4). ^{13}C NMR: 13.7 (C-10), 22.7 (C-9), 30.1 (C-8), 51.1 (OCH_3), 116.3, 128.3, 128.6, 136.9, 137.5, 145.0 (C-2–C-7), 166.9 (CO_2CH_3). UV: λ_{max} 299 nm (ε 37656). HRMS for $C_{11}H_{12}O$ calcd 180.1150, found 180.1153.

3.1.5. Methyl (*E,E,E*)-2,4,6-decatrienoate (6). Acetal **5** (215 mg, 1.26 mmol) was deprotected with *p*-toluenesulphonic acid monohydrate (5 mg) in a mixture of water (2.5 mL) and acetone (6 mL) at 0–5 °C as described for acetal **2**. Crude (*E,E*)-2,4-octadienal (143 mg) was added to a mixture of trimethyl phosphonoacetate (306 μL, 1.9 mmol), potassium carbonate (435 mg, 3.15 mmol) and water (315 μL). The mixture was stirred overnight protected from light, diluted with water, and extracted with hexanes/ether, 1:1. The organic extracts were washed with brine and dried with Na_2SO_4. After evaporation of the solvent, the crude product was purified by flash chromatography with hexanes/ethyl acetate, 95:5, to afford ester **6** (172 mg, 76%) containing 5% **3**. MS (*m/z*): 180 (M^+, 57), 151 (10), 149 (19), 138 (19), 121 (24), 120 (17), 119 (49), 111 (20), 107 (31), 106 (15), 105 (19), 91 (84), 79 (100), 77 (38). ^{1}H NMR: 0.91 (t, J=7.2 Hz, H-10), 1.44 (sextet, J=7.3 Hz, H-9), 2.12 (br q, J=7.1 Hz, H-8), 3.73 (s, OCH_3), 5.83 (d, J=15.5 Hz, H-2), 5.93 (dt, J=15.1, 6.8, H-7), 6.13 (br dd, J=10.6, 15.1 Hz, H-6), 6.20 (dd, J=14.8, 11.3 Hz, H-4), 6.53 (dd, J=14.8, 10.5 Hz, H-5), 7.29 (dd, J=15.5, 11.4 Hz, H-3). ^{13}C NMR: 13.7 (C-10), 22.1 (C-9), 35.0 (C-8), 51.4 (OCH_3), 119.5, 127.7, 129.9, 140.5, 141.3, 145.1 (C-2–C-7), 167.6 (CO_2CH_3). UV: λ_{max} 292 nm (ε 45216). HRMS for $C_{11}H_{12}O$ calcd 180.1150, found 180.1159.

3.1.6. Methyl (*Z,E,E*)-2,4,6-decatrienoate (7). Crude (*E,E*)-2,4-octadienal, prepared from acetal **5** (266 mg, 1.56 mmol) as described in the previous experiment, was dissolved in 5 mL THF and added to a Horner–Wadsworth–Emmons reagent prepared from bis(2,2,2-trifluoroethyl) (methoxycarbonylmethyl)phosphonate (332 μL, 1.57 mmol), 18-crown-6 (2.068 g, 7.83 mmol), potassium bis(trimethylsilyl)amide (3.13 mL 0.5 M in toluene, 1.57 mmol), and dry THF (40 mL) as described for ester **4**. The mixture was stirred for 1 h, then worked-up, and flash chromatographed with hexanes/ethyl acetate, 97:3, to provide (*Z,E,E*)-ester **7** (245 mg, 87%) containing 5% ester **4**. MS (*m/z*): 180 (M^+, 39), 151 (7), 149 (17), 138 (18), 121 (19), 119 (44), 107 (28), 91 (82), 79 (100), 77 (37). ^{1}H NMR: 0.91 (t, J=7.4, H-10), 1.43 (sextet, J=7.3 Hz, H-9), 2.12 (br q, J=7.2 Hz, H-8), 3.72 (s, OCH_3), 5.60 (d, J=11.3 Hz, H-2), 5.92 (dt, J=14.8, 7.2 Hz, H-7), 6.21 (dd, J=14.9, 10.8 Hz, H-6), 6.46 (dd, J=14.8, 10.8 Hz, H-5), 6.58 (dd, $J_1 \sim J_2$=11.3 Hz, H-3), 7.40 (dd, J=15.0, 11.8 Hz, H-4). ^{13}C NMR: 13.7 (C-10), 22.1 (C-9), 35.0 (C-8), 51.0 (OCH_3), 115.7, 126.5, 130.4, 140.4, 142.2, 145.2 (C-2–C-7), 167.0 (CO_2CH_3). UV: λ_{max} 297 nm (ε 35521). HRMS for $C_{11}H_{12}O$ calcd 180.1150, found 180.1154.

3.1.7. 2,4-Octadiyn-1-ol (8). 3-Bromo-1-propyn-1-ol was prepared from propargyl alcohol (11.20 g, 0.20 mol) and sodium hypobromide.[26] The crude product was extracted with ether, dried (Na_2SO_4), concentrated under reduced pressure and used in Cadiot–Chodkiewicz[27] condensation without further purification. The reaction flask was charged under N_2 atmosphere with a 30% solution of *n*-$BuNH_2$ (167 mL), cooled to 0–5 °C and CuCl (1.00 g, 10.1 mmol) and NH_2OH hydrochloride (3–4 g) were added. 1-Pentyne (16.32 g, 0.24 mol) was added at once followed by slow addition of 3-bromo-1-propyn-1-ol at 5–15 °C. More NH_2OH hydrochloride was added (total 16.68 g, 0.24 mol) throughout the addition of bromopropynol to prevent the solution from turning blue. The reaction mixture was stirred another 45 min after the addition of bromopropynol, then the layers were separated, and the aqueous phase was extracted with ether. The combined ethereal extracts were washed with NH_4Cl, 3% HCl, brine and dried (Na_2SO_4). After evaporation of the solvent, the crude material was filtered through silica gel aided with hexane/ethyl acetate, 10:1, to give pure 2,4-octadiyn-1-ol (12.51 g, 51% from propargyl alcohol). MS (*m/z*): 122 (M^+, 46), 107 (18), 91 (25), 79 (44), 77 (100), 65 (30), 63 (26), 51 (15), 39 (32). ^{1}H NMR: 0.98 (t, J=7.4 Hz, H-8), 1.55 (sextet, J=7.3 Hz, H-7), 1.83 (OH), 2.25 (t, J=7.2 Hz, H-6), 4.30 (br s, H-1). The data are in close agreement with those reported.[28]

3.1.8. (*Z,Z*)-2,4-Octadien-1-ol (9). Compound **8** (2.44 g, 20.0 mmol) was stirred with 3,4-dihydro-2*H*-pyran (2.52 g, 30.0 mmol) in the presence of pyridinium *p*-toluenesulfonate (503 mg, 2.0 mmol) in a methylene chloride solution (50 mL) at 25 °C for 4 h. Evaporation of the volatiles and subsequent flash chromatography with hexanes/ethyl acetate, 12:1, gave tetrahydro-2-[(2,4-octadiynyl)oxy]-2*H*-pyran (3.74 g, 18.1 mmol, 91% yield). This was dissolved in dry THF (10 mL) and added at −20 °C to a suspension of dicyclohexylborane in THF prepared as follows: Borane–methyl sulfide complex (4.03 mL of 10 M in THF, 40.3 mmol) was added under N_2 atmosphere to dry THF (55 mL) at 0 °C, followed by addition of cyclohexene (8.2 mL, 81 mmol) and stirring for 0.5 h at 5–10 °C and 2 h

at rt. After the addition of the THP ether, the mixture was warmed to rt, stirred for 22 h, quenched with glacial acetic acid (20 mL) at 0 °C, and stirred at rt for 20 h. The solution was cooled to 0 °C and treated with 5 M NaOH (82 mL), then 30% H_2O_2 (10 mL) upon which the temperature went up and was maintained at ~30 °C for 1 h. The mixture was poured into water (100 mL), extracted with hexanes/ether, 1:1, then the combined organic extracts were washed with NH_4Cl solution and dried (Na_2SO_4). Evaporation of the solvent and flash chromatography with hexanes/ethyl acetate, 20:1, afforded (2*Z*,4*Z*)-tetrahydro-2-[(2,4-octadienyl)oxy]-2*H*-pyran (2.889 g, 76%), which was deprotected by heating with pyridinium *p*-toluenesulfonate (340 mg) in methanol (20 mL) at 50–55 °C. The solution was concentrated, dissolved in ether/hexanes, 1:1, washed with brine, dried, and flash chromatographed with pentane/ethyl acetate, 5:2, to yield (*Z*, *Z*)-2,4-octadien-1-ol (1.560 g, 90%; 62% yield from 2,4-octadiyn-1-ol, 99% purity by GC). MS (EI, *m/z*): 126 (M^+, 23), 108 (19), 93 (21), 82 (36), 83 (100), 84 (60), 79 (87), 77 (42), 70 (39), 69 (30), 67 (84), 55 (89). ^{1}H NMR ($CDCl_3$): 0.90 (t, J=7.3 Hz, H-8), 1.40 (sextet, J~7.4 Hz, H-7), 2.15 (br q, J=7.4 Hz, H-6), 4.31 (br d, J=6.8 Hz, H-1), 5.49–5.64 (m, 2H, H-2, H-5), 6.23 (dd, $J_1 \sim J_2$=11.3 Hz, H-3), 6.37 (dd, J=11.7, 10.6 Hz, H-4). ^{13}C NMR (76 MHz, $CDCl_3$): 13.7 (C-8), 22.7 (C-7), 29.4 (C-6), 58.6 (C-1), 122.9, 125.8, 129.1, 134.4 (C-2–C-5). HRMS for $C_8H_{14}O$ calcd 126.1045, found 126.1043.

3.1.9. Methyl (*E*,*Z*,*Z*)-2,4,6-decatrienoate (10) and methyl (*Z*,*Z*,*Z*)-2,4,6-decatrienoate (11). Activated manganese dioxide (Alfa Aesar, technical grade, Ward Hill, MA, 1.74 g, 20 mmol) was added under N_2 to a solution of dienol **9** (252 mg, 2 mmol) and methyl (triphenylphosphoranylidene)acetate (803 mg, 2.4 mmol) in dry methylene chloride (30 mL). The flask was protected from light by wrapping in aluminum foil, and the mixture was stirred for 12 h at 25 °C, or until TLC showed no intermediate aldehyde present. The mixture was filtered through a short pad of Celite under N_2 pressure aided with an additional amount of CH_2Cl_2 (3×10 mL). The filtrate was then concentrated and flash chromatographed with hexanes/CH_2Cl_2, 1:1. A mixture of **10** and **11** (253 mg, 70%) was isolated and carefully re-chromatographed using hexanes/ethyl acetate, 19:1, to first afford ester **11** (13 mg). MS (*m/z*): 180 (M^+, 63), 151 (10), 149 (11), 138 (20), 137 (11), 121 (25), 120 (18), 119 (44), 111 (18), 107 (28), 105 (30), 93 (21), 91 (100), 79 (87), 77 (38). ^{1}H NMR: 0.92 (t, J=7.3 Hz, H-10), 1.43 (sextet, J=7.3 Hz, H-9), 2.22 (br q, H-8), 3.72 (s, OCH3), 5.69 (d, J=11.2 Hz, H-2), 5.72 (m, H-7), 6.55 (dd, $J_1 \sim J_2$=11.3 Hz, H-3), 6.67 (dd, $J_1 \sim J_2$= 11.5 Hz, H-5), 7.10 (dd, J=12.1, 11.3 Hz, H-6), 7.27 (br dd, $J_1 \sim J_2$=11.5 Hz, H-4). ^{13}C NMR: 13.7 (C-10), 22.6 (C-9), 29.7 (C-8), 51.1 (OCH_3), 117.2, 122.7, 123.8, 132.1, 137.5, 138.6 (C-2-C-7), 166.8 (CO_2CH_3). UV: λ_{max} 303 nm (ε 26674). HRMS for $C_{11}H_{12}O$ calcd 180.1150, found 180.1146. Further elution provided a mixture of esters **11** and **10** (25 mg), and finally pure **10** (182 mg, 51%). MS (*m/z*): 180 (M^+, 68), 151 (7), 149 (7), 138 (8), 121 (21), 120 (16), 119 (26), 107 (24), 106 (30), 105 (36), 93 (27), 91 (100), 79 (73), 77 (35). ^{1}H NMR: 0.91 (t, J=7.4 Hz, H-10), 1.43 (sextet, J=7.3 Hz, H-9), 2.21 (br q, J=7.6 Hz, H-8), 3.75 (s, OCH_3), 5.73 (dt, J=9.1, 8.0 Hz, H-7), 5.88 (d, J= 15.2 Hz, H-2), 6.08 (dd, J=11.2, 9.4 Hz, H-4), 6.60 (m, 2H, H-5, H-6), 7.77 (dd, J=15.2, 11.7 Hz, H-3). ^{13}C NMR ($CDCl_3$): 13.7 (C-10), 22.6 (C-9), 29.7 (C-8), 51.5 (OCH_3), 121.1, 123.3, 125.9, 132.1, 137.4, 139.3 (C-2–C-7), 167.5 (CO_2CH_3). ^{1}H and ^{13}C NMR data matched those reported.[3] UV: λ_{max} 299 nm (ε 29214).

3.1.10. Swern oxidation–Wittig reaction of 9. To a stirred solution of oxalyl chloride (214 μL, 2.45 mmol) in CH_2Cl_2 (15 mL) was added methyl sulfoxide (348 μL, 4.95 mmol) at −60 °C. After stirring for 20 min, a solution of alcohol **9** (252 mg, 2 mmol) in CH_2Cl_2 (10 mL) was added. After 20 min, triethylamine (1.393 mL, 10 mmol) was added at −60 °C, and the mixture was allowed to warm to 0 °C. Methyl (triphenylphosphoranylidene)acetate (2.00 g, 6.0 mmol) was added at once and the mixture was stirred at room temperature for 3 h, or until TLC (CH_2Cl_2) showed essentially no intermediate aldehyde present. The mixture was poured into ice-water (30 mL) and extracted with CH_2Cl_2 (3×30 mL). The combined organic extracts were washed with water, dried (Na_2SO_4), concentrated, and chromatographed using hexanes/CH_2Cl_2, 1:1. *Z*,*Z*,*Z*-Isomer **11** (19 mg) was isolated in the first fraction and *E*,*Z*,*Z*-isomer **10** (196 mg) in the most polar fraction. ^{1}H NMR did not reveal any significant impurities in **11**, but it showed 15% contamination of **10** with *E*,*E*,*Z* isomer **3**.

3.1.11. (*E*)-4-Octen-2-yn-1-ol (12). Tetrakis(triphenylphosphine)palladium (3.11 g, 2.0 mmol) was added under N_2 to a solution of (*E*)-1-iodo-1-pentene[23] (7.84 g, 40.0 mmol) in benzene (100 mL). After 45–50 min, a solution of cuprous iodide (1.52 g, 8.0 mmol) and propargyl alcohol (3.36 g, 60.0 mmol) in *n*-butylamine (40 mL) was added over 15–20 min maintaining the temperature 20–25 °C by cooling. The resulting dark-brown mixture was stirred for 2.5 h and poured into sat. NH_4Cl (400 mL) then extracted with ether (200 mL). The organic layer was separated and the aqueous phase was extracted with ether:hexane, 1:1 (3×100 mL). The combined extracts were washed with sat. NH_4Cl, ammonium hydroxide, brine, and dried with sodium sulfate. After evaporation of the solvent, the residue was distilled under vacuum (bp 69–70 °C/0.05 mmHg) to give 4*E*-octen-2-yn-1-ol containing 4–5% of the homo-coupling product, 4,6-decadiene (MS: 138 (M^+, 45), 109 (25), 95 (28), 82 (19), 81 (30), 67 (100), 55 (13), 54 (14). The product was further purified by flash chromatography with hexane/ethyl acetate, 3:1, to give 98% pure **12** (3.482 g, 69%). MS (*m/z*): 124 (M^+, 100), 95 (39), 91 (43), 81 (96), 79 (50), 77 (41), 67 (30), 65 (56), 55 (35). ^{1}H NMR: 0.89 (t, J=7.2 Hz, H-8), 1.41 (sextet, J=7.2 Hz, H-7), 2.07 (br q, J=7.2 Hz, H-6), 4.35 (br s, H-1), 5.48 (dm, H-4), 6.15 (dt, J=15.5, 7.2 Hz, H-5). HRMS for $C_8H_{12}O$ calcd 124.0888, found 124.0888. **12** was described in the literature[29] as a mixture with *Z* isomer.

3.1.12. (*Z*,*E*)-2,4-Octadien-1-ol (13). Alcohol **12** (1.84 g, 14.8 mmol) was reduced with Zn(Cu/Ag) prepared from zinc (29.25 g, 0.447 mol), copper(II) acetate hydrate (2.925 g) and silver nitrate (2.925 g) in methanol at 40–43 °C for 8 h as described.[24] The crude product (1.695 g) was distilled under vacuum to provide >98% pure 2*Z*,4*E*-octadien-1-ol (1.495 g, 80%). Bp 53 °C/0.05 mmHg. MS (*m/z*): 126 (M^+, 32), 108 (16), 93 (14) 91 (14), 84 (51), 83 (100), 82 (29), 79 (65), 77 (33), 70 (36), 69 (28), 67 (72), 55

(83). ^{1}H NMR: 0.90 (t, J=7.4 Hz, H-8), 1.41 (sextet, J=7.3 Hz, H-7), 2.08 (q, H-6), 4.29 (br d, J=6.9 Hz, H-1), 5.48 (dt, J=10.6, 7.1 Hz, H-2), 5.74 (dt, J=14.4, 7.2 Hz, H-5), 6.06 (dd, J_1=J_2=10.7 Hz, H-3), 6.30 (dd, J=14.7, 11.0 Hz, H-4). HRMS for $C_8H_{14}O$ calcd 126.1045, found 126.1041. **13** was described in the literature as a mixture with *Z*,*Z* isomer and characterized by ^{13}C NMR.[29]

3.1.13. Methyl (*E*,*Z*,*E*)-2,4,6-decatrienoate (14) and methyl (*Z*,*Z*,*E*)-2,4,6-decatrienoate (15). Manganese dioxide (3.82 g, 43.9 mmol) was added under N_2 in five portions over 5 h to a solution of dienol **13** (553 mg, 4.39 mmol) and methyl (triphenylphosphoranylidene)acetate (1.91 g, 5.71 mmol) in dry methylene chloride (60 mL). The mixture was stirred for another 16 h at 25 °C and filtered through a short pad of Celite. The filtrate was concentrated and flash chromatographed with hexanes/CH_2Cl_2, 1:1 to afford: *Z*,*Z*,*E* ester **15** (24 mg, 3%), a mixture of **15** and **14** (164 mg) and *E*,*Z*,*E* ester **14** (467 mg, 59%).

Ester **15** was 93% pure by GC and was contaminated with isomers **14** and **7**. Spectral data for **15**: MS (*m*/*z*): 180 (M^+, 71), 151 (13), 149 (14), 138 (27), 137 (15), 121 (29), 119 (70), 111 (25), 107 (37), 91 (100), 79 (87), 77 (36). ^{1}H NMR: 0.91 (t, J=7.3 Hz, H-10), 1.45 (sextet, J=7.4 Hz, H-9), 2.14 (br q, J=6.9 Hz, H-8), 3.72 (s, OCH_3), 5.66 (br d, J=11.7 Hz, H-2), 5.97 (dt, J=15.0, 7.2 Hz, H-7), 6.33 (dd, $J_1 \sim J_2$=11.3 Hz, H-5), 6.58 (dd, J=14.8, 11.3 Hz, H-6), 7.09 (dd, H-3), 7.15 (br dd, H-4). ^{13}C NMR: 13.7 (C-10), 22.2 (C-9), 35.1 (C-8), 51.1 (OCH_3), 116.5, 122.3, 124.9, 137.9, 138.9, 140.7 (C-2–C-7), 166.9 (CO_2CH_3). UV: λ_{max} 298 nm (ε 35197). HRMS for $C_{11}H_{12}O$ calcd 180.1150, found 180.1145.

Isomer **14** was thermally unstable at GC injection temperature 260 °C but at 130 °C showed purity of 96%. MS (*m*/*z*): 180 (M^+, 68), 151 (12), 149 (14), 138 (18), 137 (15), 121 (27), 119 (49), 111 (20), 107 (32), 91 (100), 79 (95), 77 (36). ^{1}H NMR: 0.91 (t, J=7.4 Hz, H-10), 1.44 (sextet, J=7.3 Hz, H-9), 2.16 (br q, J=6.9 Hz, H-8), 3.74 (s, OCH3), 5.84 (d, J=15.1 Hz, H-2), 5.90 (dt, H-7), 5.96 (dd, H-4), 6.27 (dd, $J_1 \sim J_2$=11.2 Hz, H-5), 6.62 (ddm, J=14.7, 11.5 Hz, H-3), 7.74 (ddd, J=15.1, 11.7, 0.8 Hz, H-3). ^{13}C NMR ($CDCl_3$): 13.7 (C-10), 22.2 (C-9), 35.1 (C-8), 51.5 (OCH_3), 120.3, 124.2, 125.5, 137.8, 139.6, 140.6 (C-2–C-7), 167.6 (CO_2CH_3). UV: λ_{max} 296 nm (ε 32984). HRMS for $C_{11}H_{12}O$ calcd 180.1150, found 180.1144.

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